

PCT/NL 2004 /000839  
NL 04/00839

REC'D 24 JAN 2005  
WIPO PCT

PA 1258704

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

December 13, 2004

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM  
THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK  
OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT  
APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A  
FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: 60/526,994

FILING DATE: December 05, 2003

PRIORITY  
DOCUMENT

SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1(a) OR (b)

By Authority of the  
COMMISSIONER OF PATENTS AND TRADEMARKS

L. Edele

L. EDELEN  
Certifying Officer



PTO/SB/16 (10-01)  
 Approved for use through 10/31/2002. OMB 0651-0032  
 U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE  
 Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.  
**PROVISIONAL APPLICATION FOR PATENT COVER SHEET**  
 This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).  
 Express Mail Label No.  

19587 U.S.PTO  
 60/526994  
  
 120503

<b>INVENTOR(S)</b>		
Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
JACOBUS WILHELMUS MARIA KINSUK	NOORDERMEER NASKAR	Nieuwstadt, The Netherlands Enschede, The Netherlands
<input type="checkbox"/> Additional inventors are being named on the _____ separately numbered sheets attached hereto		
<b>TITLE OF THE INVENTION (500 characters max)</b>		
PROCESS FOR THE PREPARATION OF A THERMOPLASTIC ELASTOMERIC VULCANIZATE		
<i>Direct all correspondence to:</i> <b>CORRESPONDENCE ADDRESS</b>		
<input checked="" type="checkbox"/> Customer Number <b>00909</b> <span style="margin-left: 20px;">→</span> <input type="checkbox"/> OR <span style="margin-left: 100px;">Type Customer Number here</span>		<span style="border: 1px solid black; padding: 2px;">Place Customer Number Bar Code Label here</span>
<input type="checkbox"/> Firm or Individual Name		
Address		
Address		
City	State	ZIP
Country	Telephone	Fax
<b>ENCLOSED APPLICATION PARTS (check all that apply)</b>		
<input checked="" type="checkbox"/> Specification Number of Pages <b>20</b>		<input type="checkbox"/> CD(s), Number <span style="border: 1px solid black; padding: 2px;"> </span>
<input type="checkbox"/> Drawing(s) Number of Sheets <span style="border: 1px solid black; padding: 2px;"> </span>		<input type="checkbox"/> Other (specify) <span style="border: 1px solid black; padding: 2px;"> </span>
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76		
<b>METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT</b>		
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. <input type="checkbox"/> A check or money order is enclosed to cover the filing fees <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: <b>033975</b> <input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.		<b>FILING FEE AMOUNT (\$)</b> <span style="border: 1px solid black; padding: 2px; width: 50px;">160.00</span>
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government. <input checked="" type="checkbox"/> No. <input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____		

Respectfully submitted  
 SIGNATURE Richard A. Steinberg  
 TYPED or PRINTED NAME Richard A. Steinberg  
 TELEPHONE (703) 905-2039

Date **Dec 5, 2003**  
 REGISTRATION NO.  
 (if appropriate)  
 Docket Number:  
26588  
030268-0307171

### **USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT**

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S.D Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

PE21749

- 1 -

PROCESS FOR THE PREPARATION OF A THERMOPLASTIC ELASTOMERICVULCANIZATE

The present invention relates to a process for the preparation of a thermoplastic elastomeric vulcanizate (TPV) comprising a mixture of a polyolefin and a vulcanized rubber, in which the vulcanization of the rubber is performed at elevated 10 temperature under the influence of a peroxide.

Such a process is disclosed in EP-A-72,203.

The emergence of thermoplastic elastomers (TPEs) in the 1950s provided a new horizon to the field of polymer science and technology. A TPE is a 15 rubbery material with properties and functional performance similar to those of conventional vulcanized rubber at ambient temperature, yet it can be processed in a molten condition as a thermoplastic polymer at elevated temperature. The sort of TPEs based on polyolefin rubber/thermoplastic polymer compositions has grown along two distinctly different product-lines or classes: one class consists of simple blends and is commonly designated as thermoplastic elastomeric olefins (TEO); in the other class, 20 the rubber phase is (dynamically) vulcanized, giving rise to a thermoplastic vulcanizate (TPV). Morphologically, TPVs are characterized by the presence of finely dispersed crosslinked rubber particles distributed in a continuous thermoplastic matrix. If the elastomer particles of such a blend are small enough and if they are sufficiently vulcanized, then the physical and chemical properties of the blend are generally 25 improved.

TPVs based on polypropylene (PP) and EPDM-rubber blends are the most important representatives of this class of materials. Several crosslinking agents are employed to crosslink the EPDM rubber in PP/EPDM blends. Each and every crosslinking system has its own merits and demerits. Crosslinking systems often used 30 for that purpose are activated phenol-formaldehyde resins, commonly known as resols. However, there are two major problems associated with TPVs based on these resol resins:

- (a) hygroscopicity, even at ambient temperature; the absorbed moisture must be removed through lengthy, high-temperature drying procedures before processing,
- 35 to eliminate product defects; and
- (b) appearance of a very dark brownish color, which is difficult to mask and sometimes necessitates the use of two different pigment systems to achieve a

- 2 -

desired color.

These disadvantages of the resols impose a demand for alternative crosslinking agents. Crosslinking of rubber with peroxides has been well known for more than fifty years. The general advantages of peroxides as crosslinking agents are:

- 5 their ability to crosslink unsaturated as well as saturated elastomers; good high temperature resistance and good elastic behaviour (compression set), particularly at elevated temperature, no moisture uptake, and no staining or discoloration of the finished products. A co-agent is often used to improve the crosslinking efficiency of the peroxide by a tighter network formation.

- 10 Besides the advantages of peroxides, there are also disadvantages. Depending on the composition of the peroxide applied, the decomposition products are more or less volatile. The latter often provide a typical smell, show a blooming effect or can be extracted from the crosslinked compound by solvents. For instance, the typical sweet smell of acetophenone, one of the decomposition products of dicumyl peroxide (DCP) is well known. Also blooming phenomena take place due to the formation of dihydroxy isopropyl benzene from the decomposition of di(tert-butylperoxyisopropyl)-benzene.

- 15 The use of a peroxide also negatively influences the physical properties of the final TPV, as the peroxide also reacts with the polyolefin used as the matrix. In the case the polyolefin is a polyethylene, the peroxide can cause crosslinking of the polyethylene, as a result of which the processability is reduced. In the case the polyolefin is a polypropylene, the peroxide can cause degradation of the polymer chain, with detrimental effect on the mechanical properties.

- 20 To overcome the above problems, a new process has been found, which reduces or even eliminates them.

25 The process according to the present Invention is characterized in that the peroxide, that is used for the vulcanization of the rubber is an organic peroxide having at least one terminal carbon-carbon double bond in the molecule.

- 30 In the following the ingredients and the process conditions used for the preparation of the TPV will be discussed.

#### A. The polyolefin

The polyolefin resin in a TPV is selected from the group comprising one or more polyolefins originating from a (co-)polymerization of an  $\alpha$ -olefin, such as

- 3 -

- ethylene, propylene, butene-1 and others, as well as the crystalline polycycloolefins. They have to behave like a thermoplastic and have a DSC crystallinity of at least 15%. A preference is present for homo- and copolymers of polyethylene and polypropylene; in the case of copolymers of said polyolefins the content of ethylene resp. propylene in  
5 said copolymer is at least 75 wt%.

**B. The rubber**

The rubber in the TPV used according to the present invention can be any rubber known in the art, provided that the rubber is peroxide crosslinkable. For  
10 an overview of peroxide vulcanizable rubbers, the reader is referred to the article of Peter R. Dluznieski, in Rubber Chem. Techn., 74, 451 ff, 2001. Rubbers preferably useful are rubbers selected from the group comprising ethylene/α-olefin copolymer rubber (EAM) as well as ethylene/α-olefin/diene terpolymer rubber (EADM) and acrylonitrile/butadiene rubber (NBR); and its hydrogenated form (HNBR). The rubber  
15 can also be a styrene based thermoplastic elastomer (STPE). An STPE is a styrene blockcopolymer of the form A-B-A, in which A is a polystyrene chain and B a polydiene chain, such as polybutadiene or polyisopropene. The polystyrene may also be based on substituted styrenes, like α-methylstyrene. The styrene/diene molar ratio generally ranges from 50/50 to 15/85. A preferred form of STPE is at least one of styrene-  
20 butadiene-styrene blockcopolymers (SBS) and their partially or fully hydrogenated derivatives (SEBS), another preferred form of STPE is a triblock copolymer based on polystyrene and vinyl bonded polyisoprene, and the (partially) hydrogenated derivatives thereof (such copolymers commercially being available from Kraton Polymers). Also polystyrenic blockcopolymers like polystyrene block-poly(ethylene-co-propylene)-block  
25 polystyrene (SEEPS or SEPS), can be advantageously applied. In the case of an EAM or EADM rubber, the α-olefin in such a rubber is preferably propylene; in such a case the rubber is referred to as EP(D)M. It is also possible to use a mixture of the above mentioned rubbers.

**30 C. The TPV**

The TPV is a family of thermoplastic elastomers comprising a blend of the (semi-)crystalline polyolefin resin and the rubber dispersed in said resin. In general these blends comprise from 15-85 parts by weight of the polyolefin resin and correspondingly from 85-15 parts by weight of the rubber.

- 4 -

In the TPV the dispersed rubber is at least partially cured (i.e. vulcanized). Generally, the rubber in the TPV has a degree of vulcanization such that the amount of extractable rubber from the TPV (based on total amount of curable rubber) is less than 90%. The test to determine such an extractable amount is 5 generally done with a solvent in which the polyolefin as well as the not-vulcanized rubber are soluble. A suitable and preferable solvent is boiling xylene.

To enjoy the best effects of the vulcanization, the TPV is preferably vulcanized to the extent that the amount of extractable rubber is less than 15%, more preferred even less than 5%.

10

#### D. The peroxide

The peroxide to be used to vulcanize the rubber is an organic peroxide having at least one terminal carbon-carbon double bond in the molecule. Preference is given to a such a peroxide, wherein the peroxide is an allyl functional 15 peroxide. Examples of such type of peroxides can be found in EP-A-250,024.

It has been found that beneficial effects on mechanical properties as well as on the attack by the peroxide on the polyolefin are obtained, when the peroxide has a relative solubility ( $\delta_r$ ) of at least 1, wherein  $\delta_r$  is the ratio between the solubility-parameter of the peroxide ( $\delta_{per}$ ) and the solubility-parameter of the polyolefin ( $\delta_{po}$ ), both 20 determined at 453 K.

The solubility parameter  $\delta_r$ , and especially the  $\delta_{per}$  and the  $\delta_{po}$ , are calculated using group contribution methods, based on the assumption that the contributions of different functional groups to this thermodynamic property are additive (see: A.F.M. Bratton, "Handbook of Solubility Parameters and Other Cohesion 25 Parameters", CRC Press, Boca Raton, 1985). Using the values of molar attraction constants given in P.A. Small, J. Appl. Chem. 3, 71 (1953), the solubility parameters of the different peroxides and polymers can be calculated for 298 K. In order to correlate these values at 298 K with the temperature under vulcanization conditions, the solubility parameter values of the peroxides at 453 K are calculated using the following 30 equation:

$$\ln \delta_r \approx \ln \delta_{298} - 1.25\alpha (T-298)$$

- (1) -

where  $\alpha$  = the co-efficient of linear thermal expansion of the pertinent compound

- 5 -

and T = 453 K. These  $\alpha$ 's are estimated from density measurements up to 353 K (see: A.H. Hogt, Proceedings of the Conference on Advances in Additives and Modifiers for Polymer) and are about  $10^{-3}$  K<sup>-1</sup>. The solubility parameter values of the polymers (polyolefin and rubber) at 453 K are calculated using the following equation:

5

$$\ln \delta_T = \ln \delta_{298} - \alpha (T-298) \quad - (2) -$$

(see S. Krause, in "Polymer Blends" (Eds. D.R. Paul and S. Newman), Vol. 1, Academic Press, New York, 1978, p. 15-113); where T = 453 K.

10           The co-efficient of linear thermal expansion for polypropylene has a value of  $6.3 \times 10^{-4}$  K<sup>-1</sup>; for EPDM said value is  $2.3 \times 10^{-4}$  K<sup>-1</sup> (see: D. W. Van Krevelen, "Properties of polymers, their correlation with chemical structure; Their numerical estimation and prediction from group additive contributions", Elsevier, Amsterdam, 1990, p. 189-225; and G. VerStrate, "Ethylene-Propylene Elastomers" in Encyclopaedia of Polymer Science and Engineering, Vol. 6, 6th ed., John Wiley & Sons, 1986, p. 522-564). The  $\delta$ -values at 453 K calculated for DCP, DTBT, TBCP and TBIB (peroxides used in the Examples and comparative experiments, see Table I), are 14.6, 19.6, 13.8 and  $12.7 (\text{J/cm}^3)^{1/2}$  respectively, whereas those of EPDM and PP are 16.6 and  $15.1 (\text{J/cm}^3)^{1/2}$ . The ranking of these  $\delta$ -values is graphically depicted in Figure 1.

20           From all these  $\delta$ -values it can be deduced, that there is a tendency for TBIB, TBCP and DCP to preferably partition towards the polyolefin phase, as compared to DTBT which will show a preference towards the EPDM-phase.

25           More preferred, the  $\delta$ , has a value of at least 1.2. Even more preferred, the  $\delta_{\text{per}}$  is at least equal to the solubility parameter of the rubber ( $\delta_{\text{rub}}$ ); or in formula form:

$$\delta_{\text{per}} \geq \delta_{\text{rubber}} \quad - (3) -$$

30           The beneficial effect of the use of a specific peroxide as per the present invention is preferably obtained when the peroxide has at least two carbon-carbon double bonds in the molecule. Another preference is in the use of a peroxide having a triazine nucleus in its molecule.

The amount of peroxide to be used is generally between 0.01 and 15 parts by weight per 100 parts of rubber. Preferably, the amount is 0.5-5.0 parts.

- 6 -

Next to the use of the specific peroxides as indicated above, the crosslinking can be influenced by the use of known crosslinking co-agents, as such known in the art. A preference is given for those co-agents, which solubility parameter ( $\delta_{\infty}$ , determined in the same way as all the other solubility parameters mentioned before) is at least equal to the  $\delta_{po}$ , and even more preferred at least equal to the  $\delta_{rub}$ .  
5 TAC with its very high  $\delta$ -value, possibly added as a co-agent, preferably ends up in the rubber-phase, and therefore boosts the effect of rubber-crosslinking.

Regarding the terminal carbon-carbon double bonds present in the peroxide to be used in the present invention, a further preference is given to those  
10 peroxides, with formula



- (4) -

in which both R' and R'' have these terminal carbon-carbon double bonds. Their use  
15 even further reduces the generation of volatile byproducts from those peroxides, and thus further reduces the emission of volatile decomposition products from the produced TPV.

E. The preparation of the TPV

20 The TPV can either be prepared by mixing the polyolefin with a particulate form of the vulcanized rubber or via a process known as dynamic vulcanization. In the first process, the rubber is vulcanized under as such known conditions with the specific peroxides referred to above, and thereafter the rubber size is reduced, as a result of which the particle size is generally below 10  $\mu m$ , more  
25 preferably below 1  $\mu m$ . These resulting rubber particles can than be mixed with the polyolefin in a well known manner.

More preferred, the TPV is prepared under dynamic mixing of the polyolefin, the rubber, and the peroxide, as a result of which both the mixing of the rubber in the polyolefin, as well as the vulcanization of the rubber takes place.

30 Information about dynamic vulcanization can for instance be obtained from the article of Coran & Patel in Rubber Chem. Techn., 53, 141 ff, 1980.

The process according to the present invention results in a TPV having improved properties compared to the TPV's known in the art. The unpleasant smell or blooming of the surface, assumed to be the result of volatile endproducts of

- 7 -

the peroxides of the prior art, is greatly reduced. Especially when peroxides with a  $\delta_r \geq 1$  are used, the reduction of the mechanical properties of the polyolefinic matrix is prevented.

- The TPV (prepared) according to the present invention can
- 5 successfully be used in those applications where the outstanding properties of the product, especially the high-temperature properties are of benefit. Reference can be made to automotive parts, especially under the hood (like clean air ducts, cable coating, boots and bellows, hoses), machinery, and domestic equipment. It can also be used in a hard/soft-combination, like coextrusion, sequential and 3D/2C (i.e. three
  - 10 dimensions and two components) extrusion, like for clean air ducts.

- The TPV can especially be used to prepare a foamed thermoplastic elastomeric article. To foam the TPV, any method known in the art can be used. One or more chemical as well as physical blowing agents can be used (like azodicarbonamides, low boiling hydrocarbons, water, N<sub>2</sub>, CO<sub>2</sub> or water releasing chemical compounds). The blowing agent(s) can be dry-blended or melt-blended with the TPV (provided that the blend-temperature is below the activation temperature of the blowing agent) or can be mixed in gaseous or liquid form in the molten TPV. Preferably, the TPV contains the blowing agent. The amount of blowing agent is dependent on the type of blowing agent: the more blowing gas is liberated per unit weight of blowing agent, the less is needed for a certain result. The person skilled in the art can readily ascertain the suitable effective amount of the appropriate blowing agent for the particular type of polymeric foam.

- Next to the indicated compounds, the TPV of the present invention may contain additional ingredients, in itself known to be used in thermoplastic elastomers, like fillers, colourants, (UV) stabilizers plasticizers, flow-improvers, antioxidants, etc..

The invention also relates to an article comprising a TPV obtainable with a process of the present invention.

- Applications in which the TPV of the present invention can be used
- 30 are e.g.: belt strips; patch seals; soft touch (knobs-grips); sunvisors; vent seals; carpet backing; headliners; seating; run flat tires; sporting pads; wet suits; footwear; first aid equipment; fabric backing; diapers; tapes; different toys; blankets/pads; luggage; ducting; floats/bumpers; bandaids; ear plugs; cups; pads/mattresses; office furniture.

In Poster 13 of the International Rubber Conference 2003, held in

- 8 -

- Nürnberg from June 30 to July 3, 2003, a (process for the preparation of a) TPV is described, which uses an ENB-based EPDM as the rubber having a Mooney viscosity of 52, and a polypropylene with a meltindex of 0.3 g/10 min. TBIB as well as DTBT are used as peroxides. The poster does not recognize nor indicate that it is essential that  
5 the peroxides have a terminal unsaturation, not that a preference exists for terminal unsaturated peroxide with a  $\delta_r \geq 1$ . It also fails to indicate that improves TPV's can be made based on other polyolefins and rubbers.

The invention will be elucidated by means of the following Examples and comparative experiments, which are not meant to restrict the invention.

10

#### Materials

- Ethyldene norbornene (ENB)-containing EPDM rubber, which includes 50 wt % of paraffinic oil, was obtained from DSM Elastomers B.V., the Netherlands. The EPDM contained 63 wt % of ethylene and 4.5 wt % of ENB; it had a  
15 Mooney viscosity, ML (1+4) @ 125° C of 52. Polypropylene (PP) was obtained from SABIC Polypropylenes B.V., the Netherlands. The melt flow index of the PP (measured at 503 K and 2.16 kg) was 0.3 g /10 min. Two stabilizers, Irganox® 1076 and Irgafos® 168 were obtained from Ciba Geigy. The chemical names and structures of four peroxides investigated are given in Table I as well as their decomposition temperatures  
20 corresponding to a half-life time of 1 hour, as determined in chlorobenzene solution.

- Two types of multifunctional peroxides were synthesized at Akzo Nobel Polymer Chemicals, the Netherlands. They combine peroxide and co-agent functionality in a single molecule. Two conventional peroxides, DCP and TBCP, were employed as reference due to their structural similarity with the multifunctional  
25 peroxides. They were also obtained from Akzo Nobel Polymer Chemicals, the Netherlands. Triallyl cyanurate (TAC), 50% and  $\alpha$ -methyl styrene ( $\alpha$ -MeS), 99%, were used as references for the co-agents. For DCP, TAC was used as co-agent because of the structural similarity with DTBT; where as for TBCP,  $\alpha$ -MeS was applied as co-agent due to the structural similarity with TBIB.

30

- In order to make a fair comparison among the various peroxides, care has to be taken, that with equal amounts of peroxides added per 100 grams of pure EPDM rubber, the amounts of the co-agent functionality per 100 grams of pure EPDM differ, depending on the amount of co-agent functionality provided by the peroxide itself. For example, if 15 milli-equivalents of peroxide was used, DTBT by its

- 9 -

nature having two terminal allylic groups, provides 30 milli-equivalents of co-agent functionality. This level of 30 milli-equivalents of co-agent functionality was then taken as reference and a correction was applied to make up for the lack of co-agent functionality in the other recipes by adding either TAC or  $\alpha$ -MeS, as shown in Table II.

5

Preparation of PP/EPDM TPVs

The PP/EPDM TPV compositions employed are given in Tables III and IV. The experimental variables were the concentrations of peroxide and co-agent (Table III) and the PP/EPDM blend ratio: (Table IV). All TPVs were prepared by mixing

- 10 in a batch process in a Brabender Plasti-Corder PL-2000, having a mixing chamber volume of 50 cc. The batch size was 36 grams. The mixer temperature was kept at 453-463K. A constant rotor (cam type) speed of 80 rpm was applied. First PP, stabilizers (Irganox 1076 and Irgafos 168) and EPDM rubber were mechanically melt-mixed. After 4 minutes of mixing, the co-agent, either TAC or  $\alpha$ -MeS was added, 15 followed by the peroxide. The mixing was continued for another 5 minutes to complete the dynamic vulcanization process. Immediately after mixing, the composition was removed from the mixer and while still molten, passed once through a cold two-roll mill to achieve a sheet of about 2 mm thick. The sheet was cut and pressed (2 mm thick) in a compression molding machine (WLP 1600/5 4/3 Wickert laboratory press at 473 K, 4 20 minutes and 12.5 MPa pressure). Aluminum foil was placed between the molded sheet and the press plates. The sheet was then cooled down to room temperature under pressure. Test specimens were die-cut from the compression molded sheet and used for testing after 24 hours of storage at room temperature.

25

Testing procedures

Tensile tests on the TPV's were carried out according to ISO 37 on dumb-bell shaped specimens (Type 2) using a Zwick tensile testing machine Z2020 at a constant cross-head speed of 500 mm / min. The Young's modulus was determined from the initial slope of the stress-strain curve between 0.1 and

- 30 0.25 % strain at a cross-head speed of 50 mm / min. Hardness of the samples was measured by a Zwick Hardness-meter (Shore A Type, ISO R868).

The overall crosslink density of the EPDM phase in presence of PP was determined on the basis of equilibrium solvent-swelling measurements (cyclohexane at 296 K). A 2-mm thick sample was submerged in cyclohexane. After 24

- 10 -

hours, the cyclohexane was refreshed to remove the extracted oil and organic stabilizers. After another 24 hours, the swollen sample was weighed, dried and weighed again. From the degree of swelling an overall crosslink density was calculated, as expressed by ( $v + PP$ ).

5

Examples I-VI and comparative experiments A-F

Influence of different types and concentrations of peroxides on the physical properties of TPV's at a fixed PP/EPDM blend ratio of 50 phr of PP

10 The mechanical properties of the PP/EPDM TPV's cured with various crosslinking agents at their different concentrations are given in Table III. For DTBT, there is a clear trend of increasing tensile strength with more crosslinking agent added.

An increase in the hardness values is noticed in all cases with increasing dosage of crosslinking agent (Table III). The average values of the hardness vary 15 between 60-70 Shore A. The crosslinking system DTBT, without extra co-agent added, gives higher values than the others.

Examples VII-XVI and comparative experiments G-R

20 Influence of different types of peroxides at fixed concentrations on the physical properties of TPV's with various PP/EPDM blend ratios

The mechanical properties of the PP/EPDM TPV's cured with various crosslinking agents with various blend ratios are given in Table IV. The properties corresponding to 50 phr PP were already given in Table III.

25 The data show that the tensile strength increases with increasing amount of PP. At 125 phr of PP, the multifunctional peroxide DTBT exhibits the highest tensile strength.

30 The results of elongation at break show quite different behavior for the four peroxides investigated. For DTBT, no significant dependence of elongation at break is observed for the various PP-contents.

The Young's modulus increases with increasing amount of PP; at 125 phr of PP, DTBT exhibits the highest value of Young's modulus.  $M_{500}$  also increases with increasing amount of PP. An increase in the values of hardness takes place with

- 11 -

increasing PP-content. Overall little difference is noticed between the various peroxides.

Avoidance of unpleasant smelling byproducts

5 It can be derived from Table V that DCP primarily generates cumyloxy radicals, which further decompose into acetophenone, having a typical sweet smell and highly reactive methyl radicals. Similarly, TBCP forms large quantities of acetophenone, as this compound still half resembles DCP. From the decomposition products of TBIB, it can be deduced that the amount of the aromatic alcohol and the  
10 aromatic ketone are below the detection limit (< 0.01 mol/mol decomposed peroxide); further no traces of other decomposition products could be identified. This implies that most of the initially formed aromatic decomposition products reacted with the substrate by the formation of adducts. As DTBT contains the same basic t-butyl peroxide unit as TBIB, it may be anticipated that its primary decomposition products will be similar. This  
15 also explains why the decomposition products obtained from the both multifunctional peroxides do not provide any unpleasant smell, unlike DCP.

As a result, the use of the multifunctional peroxides, like DTBT and TBIB, having both peroxide and co-agent functionality in a single molecule, provide TPV-properties, which are grossly comparable with commonly employed co-agent  
20 assisted peroxides. With co-agent TAC assisted DCP taken as reference for the overall combination of physical properties in PP/EPDM TPV's, particularly DTBT performs the better of the two. DTBT has a solubility parameter on the high side of the spectrum, which directs this peroxide/co-agent combination preferably to the EPDM-phase during mixing. The co-agent functionality of this compound helps to improve the crosslinking  
25 effect, so as to be comparable with DCP. DTBT further shows a decomposition-temperature related to a  $t_{50} = 1$  hour close to DCP, which results in a vulcanization rate, which is grossly comparable. Multifunctional peroxides might provide by-products after their decomposition, but without unpleasant smell unlike DCP.

- 12 -

Table I

CHEMICAL / COMMERCIAL NAMES, TEMPERATURE CORR. TO HALF-LIFE TIME  
OF 1 HR, AND STRUCTURES OF PEROXIDES STUDIED

5

	Chemical/ commercial name	T (K) for $t_{1/2} = 1$ hour	Chemical structure
10	1-(2-tert-Butylperoxyisopropyl)- 3-isopropenyl benzene (TBIB) (71%): multifunctional	411	
15	2,4-Diallyloxy-6-tert-butylperoxy- 1,3,5-triazine (DTBT) (95%): multifunctional	405	
20	Dicumyl peroxide (DCP) (Perkadox® BC-40B) (40%)	401	
25	Tert-butyl cumyl peroxide (TBCP) (Trigonox® T) (50%)	404	
30			

® Registered trademark of Akzo Nobel Chemicals B.V.

- 13 -

Table II

## 5 CORRECTION FOR CO-AGENT FUNCTIONALITY

	Name of peroxide	Amount of peroxide (mmol)	Peroxide functionality (meq)	Co-agent functionality (meq)	Co-agent added extra (meq)
10	TBIB	15	15	15	15 ( $\alpha$ -MeS)
	DTBT	15	15	30	—
	DCP	15	15	—	30 (TAC)
	TBCP	15	15	—	30 ( $\alpha$ -MeS)

- 14 -

Table III. TPV compositions (phr) and corresponding properties. Variation of peroxide and co-agent concentrations

Example / Comp. Exp.	I	II	III	IV	V	VI	A	B	C	D	E	F
Component												
EPDM	200	200	200	200	200	200	200	200	200	200	200	200
PP	50	50	50	50	50	50	50	50	50	50	50	50
Peroxide:												
TBIB	1.7(5)	3.4(10)	5.1(15)	-	1.5(5)	3.0(10)	4.5(15)	-	3.4(5)	6.8(10)	10.1(15)	-
DTBT	-	-	-	-	-	-	-	-	-	-	-	-
DCP	-	-	-	-	-	-	-	-	-	-	-	-
TBCP	-	-	-	-	-	-	-	-	-	-	-	-
Co agent:												
TAC	-	-	-	-	-	-	1.7(10)	3.4(20)	5.1(30)	-	1.2(10)	1.8(16)
o-MeS	0.8(5)	1.2(10)	1.8(15)	-	-	-	-	-	-	-	-	-
Stabilisers :												
Inganox 1076	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Igafos 168	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Mechanical properties												
Tensile strength (MPa)	4.0	4.1	4.3	3.0	4.3	5.2	4.7	5.5	5.1	3.4	5.1	5.3
Elongation at break (%)	685	629	650	412	593	604	548	418	368	567	617	587
Young's modulus (MPa)	10.1	11.1	12.7	13.2	14.0	18.4	16.6	19.0	21.1	11.6	15.9	19.2
Modulus 300% (MPa)	2.3	2.4	2.9	2.7	2.9	3.6	3.2	4.4	4.4	2.4	2.9	3.4
Hardness (Shore A)	60	62	64	66	67	68	63	66	68	63	63	65
Overall crosslink density ( $\text{v+PP} \times 10^5$ (mol/m <sup>3</sup> )	2.3	2.8	5.5	2.1	4.5	8.4	7.5	16.0	17.5	2.8	4.7	7.8

<sup>a</sup>Includes 50 wt % paraffinic oil<sup>b</sup>Numbers between brackets represent mill-equivalents of peroxides and co-agents per 100 parts of pure EPDM rubber

- 15 -

TABLE IV Various polyolefin-rubber ratios

Example / Comp. Component	VII	VIII	IX	X	XI	XII	XIII	XIV	G	H	I	J	K	L	M	N	O	F	Q	R
EPDM	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	
PP	25	75	100	125	25	75	100	125	25	75	100	125	25	75	100	125	25	75	100	
Peroxide:																				
TBIB	5.1	5.1	5.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
DTBT	-	-	-	4.5	4.5	4.5	4.5	-	-	-	-	-	-	-	-	-	-	-	-	
DCP	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
TBCP	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Co-agent:																				
TAC	-	-	-	-	-	-	-	-	5.1	5.1	5.1	-	-	-	-	-	-	-	-	
$\alpha$ -MeS	1.8	1.8	1.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Stabilizers:																				
Iranox 1076	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	
Irgafos 168	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	
Mechanical Properties																				
Tensile strength (Mpa)	2.6	6.8	7.0	7.3	2.3	5.3	6.8	8.6	2.2	6.2	7.8	8.1	2.2	5.6	5.8	6.8	3.4	6.2	6.7	
Elongation at break (%)	440	579	453	367	482	465	415	463	235	377	405	337	418	475	419	329	512	520	464	
Young's modulus (MPa)	2.9	45.6	93.2	115.0	1.9	43.0	80.4	134.0	3.2	54.0	80.0	123.0	2.0	30.3	49	78	3.5	44.8	81.1	
Modulus 300% (MPa)	2.0	4.7	6.1	6.9	1.6	4.4	6.1	7.4	-	5.4	6.6	7.8	1.8	4.3	5.1	6.6	2.2	4.7	5.7	
Hardness (Shore A)	37	76	85	90	34	76	86	90	42	80	87	91	40	77	86	90	38	76	85	
Overall crosslink density ( $\text{v+PP}_2\text{X}_1\text{O}_6$ (mol/m))	5.8	12.0	14.1	17.9	4.3	11.6	15.3	19.5	13.4	22.1	25.3	28.2	5.1	13.9	15.1	17.0	5.0	12.7	14.0	
																	20.1			

DSM IP GELEEN

046-4761830

NR. 1185

- 16 -

TABLE V

## RELATIVE AMOUNTS OF DECOMPOSITION PRODUCTS FROM VARIOUS PEROXIDES

	Name of peroxide	Experimental temperature (K)	Decomposition products	Relative amount (mole/mole peroxide)
5	DCP	433	Methane	0.91
			Acetophenone	0.91
			2-phenylpropanol-2	1.06
			$\alpha$ -methylstyrene	0.01
			Water	0.01
10	TBCP	428	Methane	0.57
			Acetone	0.13
			tert-Butanol	0.79
			Acetophenone	0.44
			2-Phenylpropanol-2	0.53
15	TBIB	428	Methane	0.63
			Acetone	0.11
			tert-Butanol	0.89
			1-(2-isopropanol)-3-isopropenyl benzene	< 0.01
			1-acetyl-3-isopropenyl benzene	< 0.01
20	DTBP	425	Water	0.04
			Methane	0.24
			Acetone	0.36
			tert-Butanol	1.63
			Dimer of pentadecane	0.40
25				
30				

- 17 -

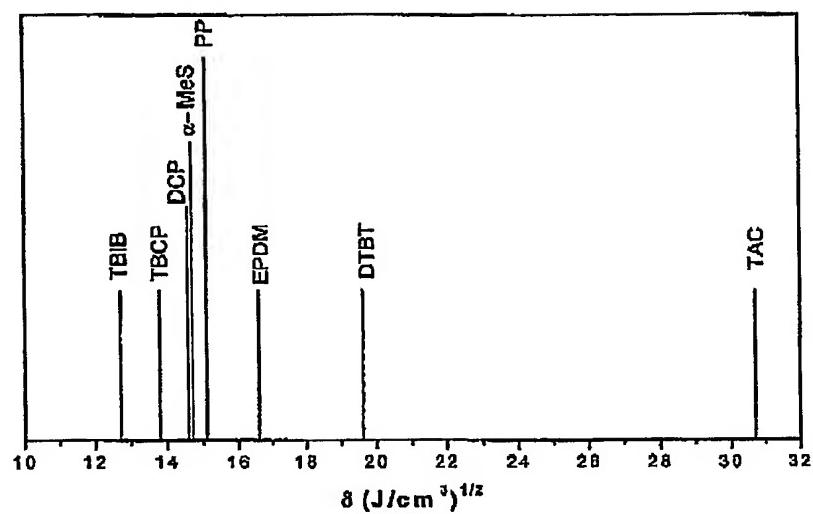


Figure 1

- 18 -

CLAIMS

1. Process for the preparation of a thermoplastic elastomeric vulcanizate (TPV) comprising a mixture of a polyolefin and a vulcanized rubber, in which the vulcanization of the rubber is performed at elevated temperature under the influence of a peroxide, wherein the peroxide is an organic peroxide having at least one terminal carbon-carbon double bond in the molecule.
5. Process according to claim 1, wherein the peroxide is an allyl functional peroxide.
10. 3. Process according to anyone of claims 1-2, wherein the peroxide has a relative solubility ( $\delta_r$ ) of at least 1, wherein  $\delta_r$  is the ratio between the solubility-parameter of the peroxide ( $\delta_{per}$ ) and the solubility-parameter of the polyolefin ( $\delta_{po}$ ), both determined at 453 K.
15. 4. Process according to claim 3, wherein  $\delta_r$  has a value of at least 1.2.
5. Process according to anyone of claims 3-4, wherein the  $\delta_{per}$  is at least equal to the solubility-parameter of the rubber ( $\delta_{rub}$ ).
6. Process according to anyone of claims 1-5, wherein the TPV is prepared via dynamic vulcanization.
7. Process according to anyone of claims 1-6, wherein the polyolefin is selected from the group comprising polyethylene and polypropylene.
20. 8. Process according to anyone of claims 1-7, wherein the rubber is selected from the group comprising EPM, EPDM, styrenic block copolymers, and (H)NBR rubber.
9. Process according to anyone of claims 1-8, wherein the peroxide has at least two carbon-carbon double bonds in the molecule.
25. 10. Process according to anyone of claims 1-9, wherein the peroxide has a triazine nucleus in its molecule.
11. Process according to anyone of claims 1-10, wherein the TPV is prepared by dynamically vulcanizing a mixture of polypropylene, EPM or EPDM, and a peroxide having a triazine nucleus in its molecule.
30. 12. Process according to anyone of claims 1-11, wherein the crosslink density of the rubber in the TPV, determined as a gel content in boiling xylene, is at least 90 %.
13. Process according to claim 12, wherein the crosslink density is at least 95 %.

- 19 -

14. Process according to anyone of claims 1-13, wherein the amount of peroxide is from 0.5 to 5.0 parts by weight per hundred parts by weight of rubber.
15. Thermoplastic vulcanizate (TPV), obtainable by a process according to anyone of claims 1-14.
- 5 16. Article, comprising a TPV of claim 15, or a TPV prepared according to a process of anyone of claims 1-14.

- 20 -

ABSTRACT

The invention deals with a process for the preparation of a thermoplastic elastomeric vulcanizate, based on a polyolefin and a rubber. The rubber  
5 is vulcanized with an organic peroxide having at least one terminal carbon-carbon bond in the molecule. As a result, blooming effects are reduced and physical properties are improved.